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Concentration cell based on electrogenic processes in the root environment

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The experimental bioelectrochemical current source based on the concentration gradient of charge carriers in the root environment of plants has been created. A potential difference of about 70 mV is observed in the nutrient solution. It is gradually decreasing due to equalization of concentrations. The voltage increases to 200 mV when plant are placed in a cultivation system as the root system develops due to the intensification of diffusion processes. The potential-forming role of nitrate forms of nitrogen is shown on the example of lettuce grown according to the panoponics technology. The separation of electrical charges by the root system during the life of plants can become an alternative source of green energy.

Keywords: rhizosphere, bioelectric potential, panoponics, green energy.

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The concentration galvanic cell is a chemical source of current composed of two identical electrodes submerged in solutions with different concentrations of the same electrolyte [1]. The main shortages of this galvanic cell are the intensive labor efforts required to prepare solutions with different concentrations and the equalization of concentrations with time that results in zero electric current in the system [2]. A promising approach can be the use of natural renewables as components of the electrochemical cell, where generation of electric current is related to the difference in concentrations of electrolyte components. The presence of natural electric fields is observed in soils, which is related to formation of different densities of mobile charges due to and under influence of soil-forming processes and caused by diffusion and adsorption of charge carriers [3], and in a soil—plant system there are gradients of concentration fields that define the migration of substances and the evolution of soils [4]. Electric charges are mobile when they are in a free soil solution or form a double electric layer on the surface of soil particles [3], i.e. a decrease in the intensity of diffusion-adsorption processes is possible with time and, as a consequence, a decrease in the potential difference in soil structures. Stability of such fields is kept by the presence of additional electromotive forces [5]: along with diffusion processes, the motion of charges can be connected with electroactivity of plants and microorganisms [6,7]. In [8] the presence of potential difference in the environment surrounding the root system was shown.

Currently bioelectrochemical devices are under development, i.e. plant microbial fuel cells (PMFC) that use as the energy resource the ability of bacteria to oxidize the rhizodeposites released by plants. The theoretically calculated maximum specific power of such cells is 3.2 W/m^2 [9] and to date a level of 679 mW/m^2 is already achieved at a 10-minute polarization, as well as a long-term generation of 240 mW/m^2 within two weeks [10].

Presumably, the electrogenic processes in the root-inhabited environment may be based on, along with the activity of electroactive bacteria, the concentration effects arising due to ion transport, which potential-forming role has never been considered before. In this case components of the nutrient medium of plants and their concentrations (presumably in the same way as properties of the electrolyte in a galvanic cell) play a critical role in the output electrical characteristics of a bioelectrochemical system based on a new concept of the use of electroactive rhizosphere processes as an energy resource. Thus, the purpose of this study is to reveal the influence of the composition of the root-inhabited environment on the formation of potential difference in the rhizosphere.

The best objects to study the electric phenomena arising in the rhizosphere are the artificial media based on nutrient solutions due to lower number of affecting external factors (first of all - humidity) and controllability of parameters (composition) of the root-inhabited environment. The Typhoon variety lettuce was selected as a phytotest object that has a well-developed tap-root system with numerous branches. The plants were grown using the technology of thin-layer panoponics [11] in the conditions of intense artifical lightculture at the biopolygon of the Agrophysical Research Institute cultivation HPS-400 lamps were use as light sources. The irradiation was 70−75 W/m^2 in the range of photosynthetically active radiation, the light period was 16 h a day, the air temperature was +20−22°C during day time and +18−20°C during night time, the relative air humidity was 65−70%. The experimental concentration cell had an area of 0.039 m^2 and a height of 0.06 m, where

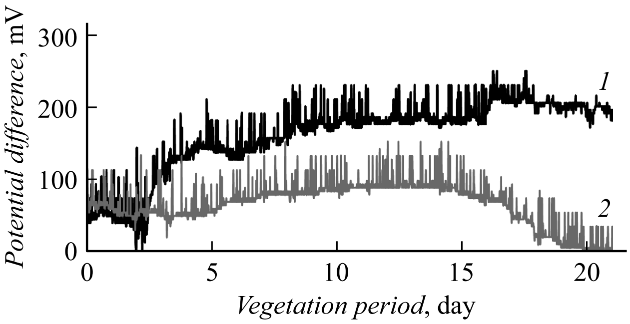

Figure 1. Potential difference in the root-inhabited environment. *1* — when cultivating lettuce plants, *2* — in the system without plants.

germinated seeds of 15 lettuce plants were accommodated and grown. The greenhouse experiment was conducted twice with three replications of the variants under study in each experiment. The data was statistically processed using the Excel 2010 program. Average values of the investigated parameters and their confidence intervals were determined. Statistical significance of difference between the variants was evaluated by parametric statistical methods (Student's *t*-test criterion). Differences between variants considered significant at $p \leqslant 0.05$.

The measured characteristic reflecting the bioelectrical activity of the root system and related microorganisms and the behavior of metabolic processes in the root-inhabited environment was bioelectric potential (BEP) i.e. the difference of potentials measured, in our case, between the root collar and the bottom of container for plant cultivation. To record BEPs formed in the root-inhabited environment, corrosion-resistant bio-friendly electrodes with large specific surface were installed in the cultivation systems [12] providing surface contact with the roots. The potential difference was monitored using the Arduino hardware platform with an interval of 15 min throughout the entire vegetation period.

In the cultivation system without plants but supplied with Knop's nutrient solution, a rise of potential difference was observed (curve *2* in Fig. 1), presumably due to the difference in concentrations of nutrient solution components at the top and bottom electrodes. The cell voltage decreased to zero with time indicating the equalization of concentrations. If plants were accommodated in the cultivating system, an increase in potential difference was observed (curve *1* in Fig. 1) probably related to the root system development, remove activity of rhizosphere microorganisms, transport of mineral substances and, as a consequence, intensification of diffusion processes.

To show up potential-forming ions, an experiment was conducted to determine the role of nutrient solution composition for the generation of bioelectric potential in the root-inhabited environment. Nitrate can act as an acceptor of electrons [13] and be reduced to N_2 with its following removal from the solution as a result of denitrification reaction [14] or to NH_4^+, which is used by the plants for biosynthesis [15]. These processes can result in competition for electrons in oxidation-reduction reactions [16]. In the literature there is ambiguous data regarding the influence of nitrogen forms in the solution on the electrical characteristics of bioelectrochemical systems. For example, in [17] it is shown that the presence of nitrate had no effect on the output power of the microbial fuel cell, while for the Spartina-based PMFC (*Spartina anglica*) with the use of modified Hoagland's solution (nitrate-free, with high content of ammonium) an increase in current by 2.5 times is reported [18], and in [19] authors reported that weekly addition of ammonium nitrate (NH_4NO_3) into a cactus-containing PMFC (*Opuntia joconostle*) increased the energy output by almost 13 times.

In this context, this work explored the following variants of the Knop's nutrient solution [20] modified by the form of nitrogen: variant 1 (classic Knop's solution) contained nitrate form of nitrogen ($Ca(NO_3)_2{\cdot}4H_2O$, KNO_3); variant *2* contained mixed nitrate-ammonium form (NH_4NO_3, KNO_3), variant 3 contained organic nitrogen (amide) form ($(NH_2)_2CO$). In each variant microelements were added according to the procedure of Chesnokov et al. [20]. The solution variants under study were equalized in terms of concentrations of nutrient elements to the maximum possible extent.

Fig. 2 shows the dynamics of potential difference in the root-inhabited environment of lettuce plants growing in nutrient solutions with different compositions. The surface contact between root ends and the electrode located at bottom of the container for cultivation at a distance of 50 mm from the root collar took place approximately on the 7–13-th day of the vegetation period. The highest BEP of 170 mV was recorded in case of growing in the Knop's solution (variant 1), with an average value of 125 mV. For variant 2 reduced values of biopotential were observed with an average value of 75 mV. No expected increase in potential difference was observed for variant 3, which did not contain a potential acceptor of electrons NO_3^-, average BEP was at a level of 50 mV. It is interesting to note the faster decrease in BEP for variants 2 and 3 containing ammonium nitrogen - as early as on the 15-th day of the vegetation period, while

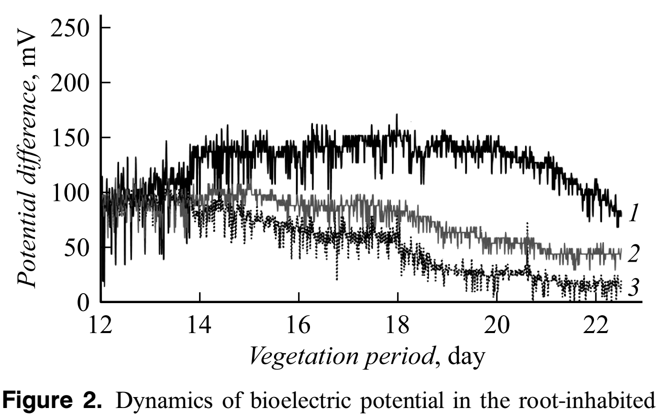

Figure 2. Dynamics of bioelectric potential in the root-inhabited environment of lettuce depending on the form of nitrogen in the nutrient solution. *1* — variant 1 (nitrate form of nitrogen), *2* — variant 2 (mixed form of nitrogen), *3* — variant 3 (organic amide form of nitrogen).

Parameters of growth and biochemical composition of vegetable products in experimental PMFC with different forms of nitrogen in the nutrient solution

Parameter	Variant of nutrient solution		
	1 (nitrate form of nitrogen)	2 (mixed form of nitrogen)	3 (organic amide form of nitrogen)
Average mass of the plant, g	18.0 ± 5.0	$13.0^* \pm 2.0$	$12.0^* \pm 2.0$
Average height of the plant, cm	19.0 ± 1.0	20.0 ± 3.0	18.0 ± 3.0
Dry substance, %	5.8 ± 0.3	6.0 ± 0.3	$5.1^* \pm 0.4$
Sum of sugars, %	15.5 ± 1.2	$18.5^* \pm 1.3$	$18.9^* \pm 1.1$
Vitamin C, mg/kg	145.2 ± 7.2	$169.4^* \pm 6.4$	$160.6^* \pm 5.8$
Nitrate, mg/kg	940.0 ± 30.0	$1157.0^* \pm 82.0$	$247^* \pm 9.8$
Total nitrogen, %	3.4 ± 0.3	3.6 ± 0.3	$4.7^* \pm 0.4$

* Value is significantly different from variant 1 at a 5-percent level of significance.

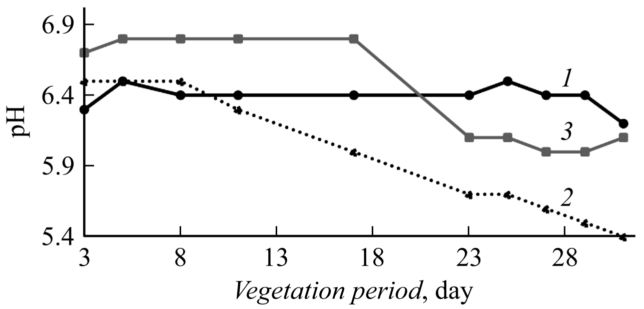

Figure 3. Change in hydrogen index pH in the root-inhabited environment in the process of plant vegetation depending on the form of nitrogen in the nutrient solution. *1* — variant 1 (nitrate form of nitrogen), *2* — variant 2 (mixed form of nitrogen), *3* — variant 3 (organic form of nitrogen (amide)).

for variant 1 the decrease in biopotential is observed only from the 20-th day of development. This period is connected to the intensive growth of aerial parts of plants [21].

In the process of plant growth, also pH values were recorded in the nutrient solution for all variants under study (Fig. 3). Some interrelation can be distinguished between the BEP dynamics and pH changes: an increase in hydrogen ions concentration in the solution (acidifying) resulted in decrease in the potential difference in the root-inhabited environment. To record possible differences in ion concentrations along the root system, pH values of water extract from the electrodes of variant 1 were measured. The top electrode was impregnated with solution with an acidity of 6.5 ± 0.1, and that for the bottom electrode was 6.1 ± 0.2. These values correspond to the polarity observed in the system: the top electrode was electrically negative and the bottom electrode was electrically positive.

The results of growth parameters and biochemical analysis of lettuce leaves grown in different nutrient solutions are presented in the table. With equal height of plants in all variants, the lettuce of variants 2 and 3 has a trend towards reduction of biomass. The presence of ammonium and amide form of nitrogen in solutions promotes the increase in content of sugars and vitamin C in the plants. As expected, considerable differences are noted in concentrations of nitrate, which are not higher than allowable concentration limits (acc. to SanPin 2.3.2.1078-01) in all variants.

Thus, the preliminary experiments showed that the best among the investigated variants of nutrient solution to produce a concentration cell based on electrogenic processes in the rhizosphere of plants growing by the panoponic method is the classic Knop's solution containing nitrogen in the nitrate form. The transfer of ions in the root-inhabited environment and separation of electric charges by the root system in the process of vital activity of plants can become a new alternative green source of electric energy.

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Conflict of interest

The authors declare that they have no conflict of interest.

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